

New applications of LC-MS and LC-MS-MS toward understanding the environmental fate of organometallics

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Abstract

Over the last 40 years, many organometallic compounds have been synthesized and used in a variety of consumer, agricultural, and industrial products. Including wastewater effluents, leaching, and direct land and water applications, there are many pathways that can disperse organometallics to the environment. Many of these compounds reach environmental compartments unchanged while others are transformed into chemical entities having different availability or toxicity to living organisms. Differences in the toxicological, biochemical, and environmental behavior of the various chemical forms of a trace-element often make the determination of the total element concentration inadequate. Considerable analytical progress in organometallic speciation has been made over the past decade, where hyphenated techniques involving highly efficient separation and sensitive detection have become the techniques of choice. Methods based on liquid chromatographic separation with mass spectrometric detection have revealed new organometallic compounds in environmental and biological matrices, contributing to a better understanding of biological effects and environmental fate of organometallics. This article surveys recent applications of liquid chromatography-mass spectrometry (LC-MS) and liquid chromatography-mass spectrometry-mass spectrometry (LC-MS-MS) for the determination of organometallic compounds in environmental matrices.

1.0 Introduction

The use of synthetic organometallic compounds in consumer, agricultural, and industrial products has grown considerably over the last four decades. Many of these synthetic compounds are important in medicine (e.g., organoplatinum as neoplastic agents; organoboron in neutron capture therapy), household products (dibutyltin, dimethyltin, octyltin in plastic formulations), agriculture (triphenyltin, fungicide; cacodylic acid as a contact herbicide; phenylarsonic acids as animal growth promoters), and in the shipping industry (tributyltin and triphenylboron as anti-molluscides) [1-4]. Biological transformation of metal or metalloid species also contributes to organometallic compounds in environmental matrices. Anthropogenic activities such as mining and the energy industry have generated biotransformed metallic compounds (methylmercury and alkyllead). Pathways for the release of organometallic compounds into the environment include wastewater effluents, leaching from landfills and plastic plumbing (PVC pipe), and direct land and water applications [5].

Awareness of the different sources and transformation pathways of organometallic compounds in the environment has increased concern about the potential toxicological effects of these compounds in living organisms. Many hold the potential for adverse effects for both aquatic organisms and humans. For example, organotin compounds show a wide spectrum of adverse effects in many species, including imposex in mollusks, neural degeneration in fetal rat cell cultures, induction of diabetes in hamsters, neurotoxicity in immature brain cell cultures, suppression of natural killer lymphocytes function, and teratogenesis if exposure is during the period of organogenesis [6-11]. While organotin derivatives are generally considered to be more toxic than the inorganic forms of the element, this is not the case for the metalloid arsenic. Biomethylation of arsenic is considered to be a detoxification mechanism used by many organisms to counteract the effects of the more toxic inorganic forms of the element. Methylarsonic acid and dimethylarsinic acid, identified in many environmental matrices, are found to be at least two orders of magnitude less toxic to mice than arsenite [inorganic arsenic (III)] and arsenate [inorganic arsenic (V)] [12]. Arsenobetaine, the most abundant and predominant arsenic species in many marine animals, has been demonstrated to have no substantial acute toxicity in laboratory test animals; its oral LD50 in mice has been estimated to exceed 10 g/kg [13]. Consumption of selenium-enriched supplements has increased dramatically as a result of reported health benefits, including protection against various forms of cancer [14-17]. The protective effect of selenium has been tentatively attributed to the biological function of selenoaminoacids [18,19]. Because of the narrow margin between essential and toxic concentrations of many selenium compounds, administration of selenium enriched products must be controlled. The toxicological and environmental impact of many synthetic organoplatinum compounds has not been studied in detail.

The differences in toxicological and biochemical properties of compounds sharing the same metal moiety, as well as their environmental mobility, make the determination of individual chemical species rather than total element concentrations necessary in many instances. Speciation analysis for

organometallic compounds is usually carried out by hyphenated analytical techniques based on the coupling of chromatography with element-selective detection. To date, the two most often used chromatographic approaches to trace-organometallic determination have been gas chromatography (GC) and high performance liquid chromatography (HPLC). For example, a hydride generation inductively coupled plasma-mass spectrometry (ICP-MS) method was developed for measuring inorganic and methylated species of As, Ge, and Sb in marine and fresh waters. Another example is the use of gas chromatography with flame photometric detection and HPLC-hydride generation inductively coupled plasma atomic emission spectrometry (HPLC-ICPAES) for measuring derivatized organotin [20-23]. Other methods call for the complexing of the organometallics, like the organotins, before analysis by HPLC-ICP-MS [24].

The use of complexing agents can produce high background interference. Methods using hydrolysis and derivatization can suffer from incomplete reactions. Newer methodologies to overcome the use of derivatization and complexation include the use of capillary electrophoresis (CE) with indirect ultraviolet and direct absorbance detection, ICP-MS with micellar liquid chromatography, and ion-exchange HPLC coupled to ICP-MS [25-29]. Currently, many organometallic and metalloid detection methods rely on hyphenated ICP-MS techniques, as thoroughly reviewed by Hill et al. [30]. However, while ICP-MS is a very sensitive mass spectrometric method, as compared with LC-MS and LC-MS-MS techniques, it still is not definitive. The mass ions produced by ICP-MS are the total metal ions, and therefore not indicative of the organic ligand(s). This is a major limitation when identification of an organometallic species is required. It is important that the analytical techniques used for organometallics not only be sensitive but provide specific speciation information. For risk assessment the exact molecular species of a compound must be determined. Advantages of LC-MS techniques over the traditional GC-based methods, and ICP-MS methods, are that no complexing agents are necessary, extraction and analysis are direct, and definitive identification of the molecular species of organometallic can be made.

This article reviews several recent applications of LC-MS and LC-MS-MS techniques for the determination of organometallic compounds in environmental matrices. For a comprehensive review of various liquid separation and mass spectrometric techniques as applied to organometallics, the reader is referred to Rosenberg [31].

2.0 LC-MS and LC-MS-MS

A brief description of LC-MS and three MS-MS techniques are described.

2.1 LC-MS

Most LC-MS applications rely upon the technique of electrospray ionization to introduce the liquid sample into the ion source. Electrospray ionization (ESI) is considered a soft ionization technique. Consequently, few ions are produced, usually the molecular ion plus some adduct ion from the mobile phase [32, 33]. To overcome this limitation it is usually necessary to perform some type of collision induced dissociation (CID), whereby an inert gas is introduced into the source and an accelerating voltage is applied to the ions in the source, producing product ions that yield structural information. However, even this technique has limitations in complex matrices, where multiple CID spectra can be produced obscuring the original precursor ion and its subsequent product ion(s). Therefore, to produce concise and specific product ions, then MS-MS techniques must be used.

2.2 MS-MS

2.2.1 Ion Traps can be used to perform CID experiments (MSⁿ) in the ion trap, and not the ion source. The precursor ion of interest is isolated in the ion trap, voltages are applied to the trapped ions inducing collisions and subsequently product ions (ions that are produced from the precursor ion). This technique produces specific product ions without the interferences from possible co-eluting chromatographic peaks, as seen in LC-MS source CID techniques, since the precursor ion is isolated from other possible co-eluting ions.

2.2.2 Orthogonal accelerating time-of-flight-mass spectrometry (oaTOF-MS) and quadrupole TOF-MS (qTOF-MS) are high mass resolution techniques capable of providing specific molecular formula identification. TOF-MS can provide full-scan spectra combined with high sensitivity and accurate mass (1 - 2 mmu). When TOF-MS is combined with quadrupole (qTOF-MS), allowing MS-MS experiments, it can provide even more structural information, thereby giving an unequivocal identification of unknown environmental contaminants. Ferrer and Thurman [34] show the usefulness of this technique in identifying unknown contaminants in complex environmental matrices.

2.2.3 With tandem mass spectrometry (MS-MS), one version of commercially available MS-MS instrumentation uses a triple quadrupole technique (QQQ). There are many configurations of the QQQ possible that use CID, as in the ion trap, but for MS-MS the Q2 (the second quadrupole) is used as a collision cell. Whether product ions, precursor ions, or neutral loss ions are monitored, all give structural information from an ionized molecule [35].

3.0 Organotin

Since LC-ESI-MS is a soft ionization technique, it is fortunate that the tin moiety (¹²⁰Sn) of organotin has 10 isotopes, thereby producing a distinctive mass cluster for each organotin compound under ESI conditions. Most researchers monitor the most abundant isotopes, ¹²⁰Sn, ¹¹⁸Sn, and ¹¹⁶Sn. Siu et al. [36] were the first to publish using atmospheric pressure chemical ionization (APCI) ionspray-tandem-MS in the selected reaction monitoring mode (SRM) for determining organotin in sediment

reference materials. Another early paper, published by Cullen et al. [37], used a Kratos MS 80 RFA mass spectrometer equipped with a Vestec Kratos thermospray interface to determine butyltins in marine samples.

Over the last decade, increasing numbers of papers show the usefulness of LC-MS and MS-MS techniques for the detection and speciation of organotins. Recent publications show the usefulness of LC-ESI-ion trap mass spectrometry (ITMS) and LC-ESI-tandem-MS in the speciation of organotins in water, fish tissue, and sediments [38-40].

4.0 Organoplatinums

Since the introduction of the catalytic converter, in the early 1980's, there has been an increase in detectable amounts of platinum in the environment [41]. The field of medicine has seen increased usage of organoplatinum compounds as anti-neoplastic drugs (e.g., cisplatin and carboplatin). Kümmerer et al. [1] note that the effluent from hospital waste should be considered as a potential source of organoplatinum in the environment. While the platinum released from catalytic converters is inorganic platinum, that released from hospital effluent would almost all be released in the organoplatinum form, thereby necessitating the use of specific speciation techniques. As organoplatinum compounds are known to be highly toxic, it would be useful for environmental risk assessment to be able to distinguish the inorganic from the organometallic species.

Two papers have recently used LC-MS-MS (QQQ instruments) to determine organoplatinum compounds in plasma [42, 43]. One analytical problem discovered is that the chlorinated platinum species tends to hydrolyze into two different species. To overcome this difficulty Oe et al. [42] used ammonium acetate with 0.1% acetic acid in the mobile phase to produce the ammonium adduct ion $[M + NH_4]^+$. They also used selected reaction monitoring (SRM) transitions and monitored the product ions, but observed an ESI suppression effect. This difficulty was overcome by using a stable isotope analog as an internal standard. Smith et al. [43], building upon the Oe et al. [42] methodology, developed a more robust method using a turbo ionspray inlet source, avoiding the ESI suppression effect. Both methods were relatively sensitive, with detection limits of 10 ppb [42] and 5 ppb [43]. Although these MS-MS applications were not applied to environmental samples, they provide information that could be readily adapted and applied to environmental matrices.

5.0 Organoboron

Organoboron compounds are used as intermediaries in various industrial processes. More recently triphenylborons are being substituted for organotins in anti-fouling paints. Triphenylborane has been shown to be extremely toxic to *Daphnia* with a 48-hr EC₅₀ of 0.002 mg/L. The oral LD₅₀ in rats is 196 mg/kg and 1236 mg/kg for triphenylborane and triphenylboron-sodium hydroxide, respectively [44]. The half-life of both compounds in a sediment model is approximately 1 year [44]. Only one article, by Hanada et al. [45], shows the quantitative determination of triphenylboron in water samples

by LC-MS. A LC-MS equipped with an ESI interface and operated in single ion monitoring (SIM) mode was used for detection and confirmation. The negative ionization mode gave the best overall sensitivity, with an instrument detection limit (IDL) of 0.011 $\mu\text{g/mL}$, corresponding to 0.023 ng/mL of triphenylboron in water. Spiked environmental waters gave recoveries from 82 to 102%; no standard deviation data was reported.

6.0 Organoselenium

The amino group(s) in selenoamino acids are readily protonated by electrospray ionization. However, because selenium is a multi-isotopic element, the ion abundance of selenoamino acids is partitioned across several m/z ratios. This makes their detection in many natural extracts almost impossible without exhaustive sample pre-concentration and clean-up.

Kotrebai and co-workers used LC-ICP-MS and LC-ESI-MS in a complementary fashion for the determination of selenium analytes in enzymatic extracts of selenized-yeast [46]. Selenomethionine was identified as the main organoselenium compound in the extracts.

Infante et al. evaluated the applicability of LC-ultrasonic nebulization (USN)-ICP-MS for the speciation of selenium compounds in enzymatic hydrolysates of selenized-yeast and Selenium MCTM tablets, and used LC-ESI-MS-MS to confirm the identity of organoselenium species present in the extracts [47]. The combination of LC-USN-ICP-MS and ESI-MS-MS allowed the identification of methylselenocysteine as a minor selenium species in the selenized-yeast and a major selenium constituent in SeleniumMCTM tablets.

Montes-Bayon et al. compared LC-ICP-MS with LC-ES-q-TOFMS as possible techniques for identifying organoselenium in plants [48]. Using LC-ICP-MS, the authors detected many species of Se-containing compounds that were previously undetected or unidentified by GC methods, but LC-ES-q-TOFMS was required to identify unknown organoselenium compounds that were revealed during the analyses. While the LC-ES-q-TOFMS method was not as sensitive as the LC-ICP-MS method, it did allow for the identification of unique organoselenium amino acids in brassica juncea.

Another unique LC-MS technique was developed for organoselenium compounds using a particle beam (PB) interface, instead of ESI, combined with glow discharge (GD) MS [49]. The researchers modified the normal electron impact-chemical ionization (EI-CI) source by replacing it with a glow discharge source. Particles impacting upon the electrode dissociated and diffused into the plasma negative glow region, where they were ionized. The authors reported ng limits of detection for three selenoaminoacids (seleno-DL-cystine, seleno-DL-methionine, and seleno-DL-ethionine), with a 5% RSD. The plasma discharge conditions can be manipulated to control the degree of fragmentation, thereby optimizing source parameters to obtain either molecular weight or molecular structure information.

In 1998 Schramel et al. [50] evaluated the utility of CE coupled on-line with ESI-MS for quantifying

selenoaminoacids. The reported limits of detection of the selenium analytes were in the range of 1 to 5 ppm. There were some limitations with this methodology, mainly concentration sensitivity (due to small injections into CE) and low efficiency in ion transport to the ESI source.

7.0 Organoarsenic

Arsenic is monoisotopic. Sensitivity is enhanced relative to organoselenium, because the ion abundance is not spread across several m/z ratios. However, a characteristic isotopic distribution no longer reveals the presence of organoarsenic ions in the mass spectrum.

ES-MS-MS can be employed such that the characteristic fragments can be observed for methylated species.

Pergantis et al. [51], reported the determination of 10 organoarsenic compounds including cacodylic acid, arsenobetaine, and the arsenic animal feed additive, 3-nitro-4-hydroxyphenylarsonic acid, also known as roxarsone (extensively used in the broiler poultry industry to promote growth by controlling coccidial intestinal parasites), by using microbore HPLC coupled with ES-MS-MS. The selectivity achieved by using tandem MS allowed for successful determination of organoarsenicals that coeluted from the HPLC column. The method was used for the analysis of an undiluted urine standard reference material (SRM) in which arsenobetaine was determined to be present at the low $\mu\text{g/L}$ level.

HPLC-ICPMS has been used in conjunction with HPLC-ES-MS to identify and quantify arsenic compounds in algal products [52, 53]. Additional applications of HPLC-ICPMS and ES-MS-MS for the identification and quantitation of organoarsenic compounds, can be found in review articles by Gong et al. and McSheehy et al. [54, 55].

A new and novel technique for analyzing organoarsenic in certified reference materials (CRM) of marine origin (biological tissue) has recently been reported [56]. This technique uses ESI-MS but to overcome the sensitivity limitations of ESI-MS, which has been repeatedly reported as a drawback to ESI-MS versus LC-ICPMS, a high-field asymmetric waveform ion mobility spectrometer (FAIMS) was inserted between the ESI interface and the MS. This allowed the authors to successfully identify two organoarsenicals previously undetected, by ESI-MS. FAIMS acts as an ion filter and has been shown to improve signal-to-noise (S/N) ratios when interfaced with mass spectrometry. Use of this technique could help overcome severe matrix interferences found in many environmental samples. Guevremont has published a review of FAIMS and various applications [57].

8.0 Other Organometallics

There are many classes of organometallic compounds. This brief review only covers some of the major classes, i.e., organotin, organoarsenic, and some of the more novel ones, i.e., organoboron and organoplatinum compounds. Finally, we would like to cover a couple of other classes not previously mentioned, either due to their scarcity in the literature or the novelty of their LC-MS and MS-MS

techniques.

The previously mentioned the PB-GD-MS method by Gibeau and Marcus [49], which was developed for determining organoselenium compounds, was also used to determine three lead compounds: lead nitrate, triethyllead chloride (TEL), and triphenyllead chloride (TphL). These three lead species, lead nitrate, TEL, and TPhL, gave detection limits of 2.98, 0.82, and 0.18 ng Pb, respectively, where the detection limits were calculated based on the response of ^{208}Pb isotope.

Another article by Dyson and McIndoe [58] examines a few very novel organometallics, using interesting variations in the ES source coupled to a quadrupole ion trap mass spectrometer. The authors analyzed for rubidium, cobalt, and tungsten organometallic complexes. They vary the ion source temperature to gain additional information regarding structure. They term this approach temperature-dependent ESI-MS. The authors found that to gain better quality spectra of these novel complexes, they needed to lower the capillary source temperatures to ambient conditions. This approach they term ambient-temperature ESI, something rarely, if ever, done during the analysis of organometallics.

9.0 Conclusions

The application of LC-MS, in combination with MS-MS, makes it a very valuable analytical tool when it comes to the analysis for organometallics. A listing of the LC-MS techniques reviewed and their applicable matrix are shown in table 1. Not only are the organometallics detected as the speciated complex, but the use of MS-MS gives much needed structural information that would not otherwise be gained by other more widely used techniques, such as ICP-MS. The trade-off for this information does seem to be in loss of sensitivity. However, the use of newer technologies coupled to LC-MS (i.e., FAIMS), as well as a better understanding of ESI processes and mass spectrometric source conditions, can often bring the detection limits (ppb to sub-ppb) for many of the organometallics well within the range of the other traditional techniques, a necessity for environmental analysis.

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Table 1 - MS-MS Techniques and their applicable matrix

MS-MS Technique	Analyte species	Environmental matrix	Reference
atmospheric pressure chemical ionization (APCI) ionspray-tandem-MS	organotin	sediment reference materials	36
thermospray (TSP) ionization-high resolution MS	butyltin	marine samples	37
electrospray ionization (ESI)-octapole ion trap MS	butyltin and phenyltin	water, fish tissue	39
ESI-quadrupole-hexapole-quadrupole-MS	butyltin and phenyltin	sediments	40
ESI-quadrupole-MS	triphenyltin and tributyltin	water	38
ESI-triple quadrupole (QQQ) MS	organoplatinum	plasma	42, 43
ESI-quadrupole-MS	triphenylboron	river water, sea water	45
ESI-q-TOFMS	organoselenium	Brassica juncea	48
particle beam-glow discharge mass spectrometry	organoselenium, alkyl lead	standards	49
capillary electrophoresis-ESI-QQQ	organoselenium	standards	50
ESI-FAIMS-ion trap mass spectrometer	organoarsenic	marine reference material (dogfish)	56

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muscle and liver, lobster
heptopancreas)